

1 Van-der-Waals approximation for real gas

The free energy of a thermodynamic system can be calculated by the formula:

$$\mathcal{F} = Nk_B T \ln (N\Lambda^3/e) - k_B T \ln Q_N \quad (1)$$

where

N is the number of particles in the system

k_B is a Boltzmann constant

T is temperature

Λ is thermal de Broigle wavelength

Q_N is configuration integral

If we neglect interactions between particles we obtain ideal gas. The free energy of an ideal gas is:

$$\mathcal{F}_{ideal} = Nk_B T \ln (N\Lambda^3/e) - Nk_B T \ln V \quad (2)$$

where V a the volume occupied by the system.

The idea of van-der-Waals approximation is to consider non-ideal gas, where particles are interacting spheres with a hard core. In that case we consider the pairwise potential:

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \sum_{j=i+1}^N u(|\mathbf{r}_i - \mathbf{r}_j|) \quad (3)$$

where the potential between two particles is defined by the expression:

$$u(r) = \begin{cases} +\infty & r < \sigma \\ u_1(r) & r > \sigma \end{cases} \quad (4)$$

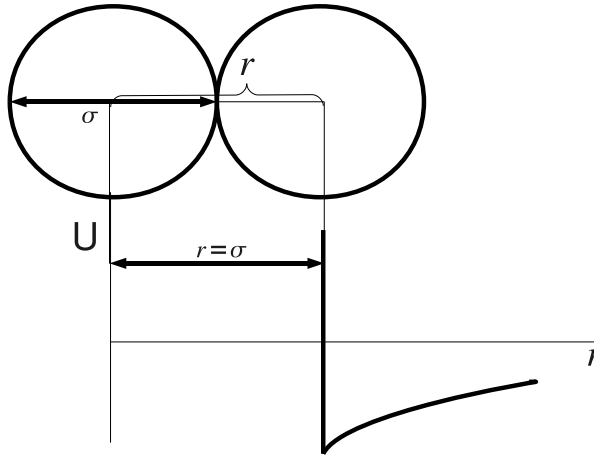


Figure 1: Potential of a spherical particles with a hard core

Example of such potential is presented on the figure (fig 1).

First, we should make a correction due to a volume of particles. In the case of potential (4) we may consider that diameter of a particle is σ . Two particles cannot be closer then sigma, so the sphere of radius σ should be excluded from the total volume. The volume of excluded sphere is $\frac{4}{3}\pi\sigma^3$ per each pair of particles. Then the excluded volume per particle is twice smaller:

$$b = \frac{2}{3}\pi\sigma^3 \quad (5)$$

Then the total "free volume" is:

$$V_f = V - Nb \quad (6)$$

Putting free volume (6) instead of total volume V into the expression (2) we obtain free energy of non-interacting hard spheres:

$$\mathcal{F}_0 = Nk_B T \ln(N\Lambda^3/e) - Nk_B T \ln(V - Nb) \quad (7)$$

Now we should account particle interactions as well. Let the gas is diluted enough that we have only pair particle collisions.

Then the total free energy is:

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2}N\psi \quad (8)$$

where

\mathcal{F}_0 is defined by (7)

ψ is the mean energy of interaction of pair of particles.

If we have an isotropic system with pairwise potential (3), the mean energy of interaction of two particles can be found by the formula:

$$\psi = 4\pi n \int_0^\infty u(r)g(r)r^2 dr = -2\frac{N}{V}a \quad (9)$$

where

n is a number density:

$$n = \frac{N}{V} \quad (10)$$

$u(r)$ is the pairwise potential (4)

$g(r)$ is radial distribution function

and constant a is defined by the equality:

$$a = -2\pi \int_0^\infty u(r)g(r)r^2 dr \quad (11)$$

Let's consider that balls are randomly distributed. The probability to find an another ball outside the given ball is equal at any distance from the ball. And, of course, balls cannot intersect and the probability to find a ball at the distance less than diameter of ball (σ) is zero.

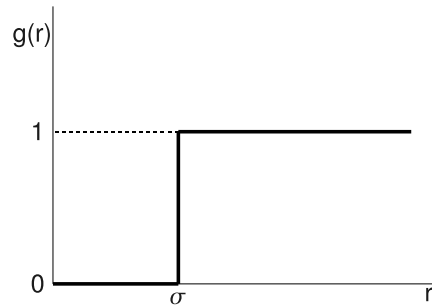


Figure 2: RDF for randomly distributed hard spheres

This assumption gives such Radial Distribution Function (see fig 2):

$$g(r) = \begin{cases} 0 & r < \sigma \\ 1 & r > \sigma \end{cases} \quad (12)$$

Considering expression for the RDF (12) and for the potential (4) the formula for the constant a (11) becomes:

$$a = -2\pi \int_{\sigma}^{\infty} u_1(r)r^2 dr \quad (13)$$

Putting expressions for the hard-spheres ideal gas energy (7) and the mean pair particles interaction energy (9) to the expression of free energy (8), we obtain the formula for the Free Energy for the van-der-Waals approximation:

$$\mathcal{F} = Nk_B T \ln \Lambda^3/e - Nk_B T \ln(V - Nb) - \frac{N^2}{V}a \quad (14)$$

where a and b are constants.

Using (14) we may find a pressure:

$$P = -\frac{\partial \mathcal{F}}{\partial V} = \frac{Nk_B T}{V - Nb} - \frac{N^2}{V^2}a = -n^2a + \frac{nk_B T}{1 - nb} \quad (15)$$

In principle, constants a and b might be defined by formulae (11), (5). However, they as well might be obtained from the macroscopic parameters of the system.

At the critical temperature derivatives of pressure over number density are equal to zero:

$$\left. \frac{dP}{dV} \right|_{T_c} = \left. \frac{d^2 P}{dV^2} \right|_{T_c} = 0 \quad (16)$$

where T_c is critical temperature

Applying it to the equation (15) we may obtain expressions for a and b :

$$b = \frac{1}{3n_c}, \quad a = \frac{9}{8} \frac{k_B T_c}{n_c} \quad (17)$$

where

T_c is critical temperature

n_c is critical number density

Putting values (17) to the pressure expression (15) we have:

$$P = -n^2 \frac{9}{8} \frac{k_B T_c}{n_c} + \frac{3nk_B T_c}{3 - \frac{n}{n_c}} = (k_B T_c n_c) \left(-\frac{9}{8} \left(\frac{n}{n_c} \right)^2 + \frac{3 \frac{n}{n_c} \frac{T}{T_c}}{3 - \frac{n}{n_c}} \right) \quad (18)$$

Let's introduce relative pressure, number density and temperature:

$$P^* = \frac{P}{P_c} \quad n^* = \frac{n}{n_c} \quad T^* = \frac{T}{T_c} \quad (19)$$

When expression (18) becomes

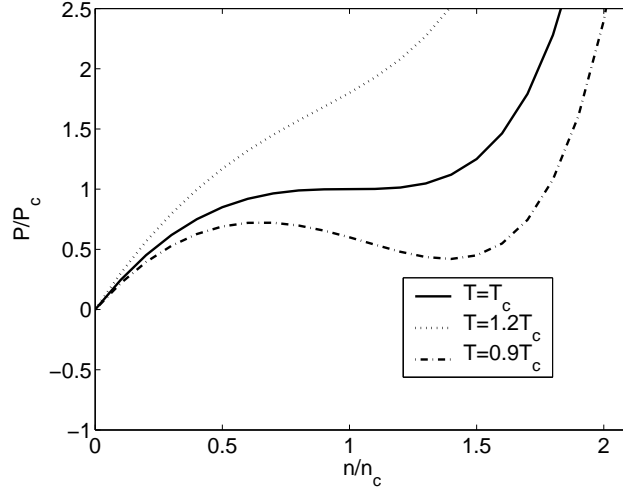
$$P^* = C \left(-\frac{9}{8} n^{*2} + \frac{3n^* T^*}{3 - n^*} \right) \quad (20)$$

where C is a constant prefactor:

$$C = \frac{k_B T_c n_c}{P_c} \quad (21)$$

The constant prefactor C might be found from (20) by putting critical conditions:

$$P^* = n^* = T^* = 1 \quad (22)$$



Under these condition we find from (20):

$$C = \frac{8}{3} \quad (23)$$

and putting it back to (20) we obtain:

$$P^* = -3n^{*2} + \frac{8n^*T^*}{3 - n^*} \quad (24)$$

We should mention, that taking to account, that free volume (6) is non-negative, all expressions are valid only then

$$n = \frac{N}{V} < \frac{1}{b} \quad (25)$$

Considering expressions (5) and (19) we may conclude, that formula (24) is valid only then $0 < n^* < 3$

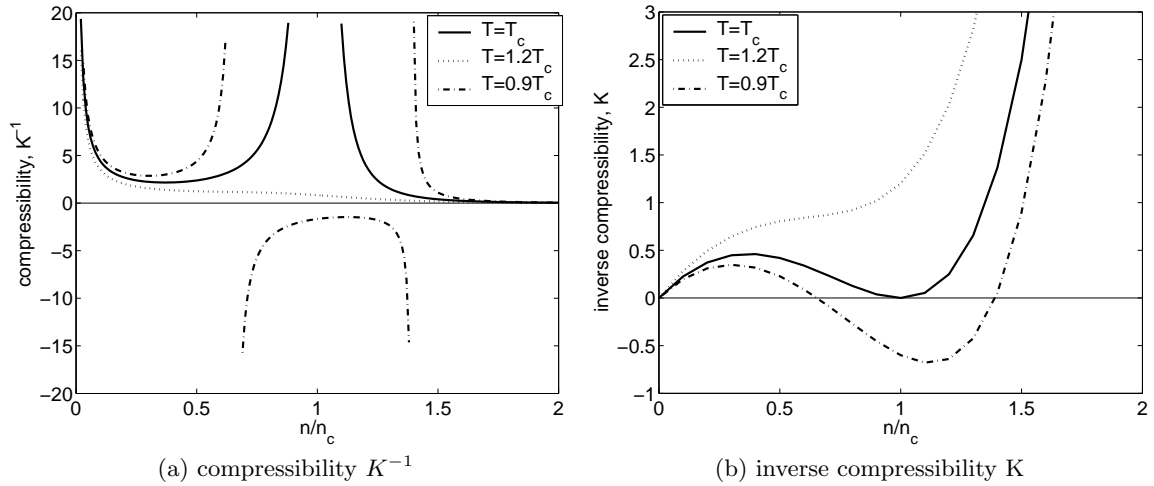


Figure 3: Dependence of of compressibility (K^{-1}) and inverse compressibility (K) on number density

Dependency of relative pressure P^* on the relative number density n^* for different relative temperatures is presented at the figure 1.

Inverse compressibility is defined by

$$K = -V \frac{\partial P}{\partial V} \quad (26)$$

It might be expressed in the terms of relative temperature and density as:

$$K = 8 \left(-\frac{3}{4} n^{*2} + \frac{1}{3} \frac{n^* T^*}{(1 - \frac{1}{3} n^*)^2} \right) \quad (27)$$

The dependence of compressibility and inverse compressibility on number density are presented on the figure 3